



RESEARCH ARTICLE

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Key Points:

- We present new measurements of BrO and OCIO at Soufrière Hills
- BrO/SO₂ during an eruption hiatus was much lower than during activity
- OCIO was detected in the plume at Soufrière Hills for the first time

Supporting Information:

- Readme
- Text01

Correspondence to:

A. Donovan,
ard31@cam.ac.uk

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Reactive halogens (BrO and OCIO) detected in the plume of Soufrière Hills Volcano during an eruption hiatus

Amy Donovan¹, Vitchko Tsanev¹, Clive Oppenheimer¹, and Marie Edmonds²
¹Department of Geography, University of Cambridge, Cambridge, UK, ²Department of Earth Sciences, University of Cambridge, Cambridge, UK

Abstract Volcanic plumes are sites of dynamic chemistry involving halogen gases. Here we present new data on the relative abundances of SO₂, BrO and OCIO gases emitted from Soufrière Hills Volcano [SHV]. They were collected during an eruptive hiatus but during sustained degassing at this halogen-rich volcano. By comparison with data from a previous study during an eruptive phase and application of the data and modeling of Villemant et al. (2008), we suggest that, after consideration of errors, either the rate of HBr conversion to BrO is variable, ranging from ~30% to ~15%, and/or the relative partitioning of Cl and Br into the gas phase from the melt changes according to eruptive activity. We examine the potential implications of this for fluid-melt partitioning, and compare our results with data from the experimental literature. Our work contributes toward understanding the controls on the BrO/SO₂ ratio for volcano monitoring purposes; the changes in plume chemistry with regard to bromine at the onset of lava extrusion may be large and rapid. OCIO was detected in the plume at SHV for the first time. This species has only previously been detected in emissions from Mount Etna (using ground-based methods) and from Puyehue Cordon Caulle (using satellite-based methods). No HCHO or NO_y species were detected in the spectra.

1. Introduction

The Soufrière Hills Volcano [SHV] on Montserrat in the West Indies has been erupting episodically since 1995 [Sparks and Young, 2002; Loughlin et al., 2010; Wadge et al., 2010]. The lava is a hornblende-hypersthene-normative andesite containing mafic enclaves of basaltic andesite composition [e.g., Murphy et al., 2000; Devine et al., 1998; Humphreys et al., 2009]. The activity to date has exhibited five eruptive phases, separated by pauses, typically of less than two years in duration until the latest pause, which began in 2010 and continues at the time of writing (July 2014). The sustained emission of SO₂ during these otherwise quiescent periods has been an important indicator of ongoing volcanic unrest [Edmonds et al., 2001; Oppenheimer et al., 2002; Christopher et al., 2010]. The Montserrat Volcano Observatory operationally measures SO₂ flux from the volcano during daylight hours, with a network of scanning UV spectrometers [Edmonds et al., 2003a, 2003b; Christopher et al., 2010] using Differential Optical Absorption Spectroscopy (DOAS), combined with meteorological information (wind velocity). Open-path Fourier-Transform Infrared (FTIR) spectroscopy is used to measure the molar ratio HCl/SO₂ in the volcanic plume [Oppenheimer et al., 2002; Edmonds et al., 2002; Christopher et al., 2010]. A key observation is that the ratio HCl/SO₂ decreases by a factor of around 10 during quiescent periods compared with periods of lava extrusion, and decreased steadily during a quiescent period [Oppenheimer et al., 2002]. The rise in HCl/SO₂ has been generally synchronous with the onset of lava extrusion and is a valuable monitoring tool [Edmonds et al., 2002; Christopher et al., 2010]. The trends have been interpreted in terms of chlorine partitioning into a hydrous vapor phase during ascent and degassing of the andesite; during pauses, little degassing of water and chlorine occurs and the plume is instead dominated by “deep-derived” SO₂ and CO₂ [Edmonds et al., 2002, 2010].

Subduction zone magmas are, in general, enriched in halogens due to the devolatilization of chlorine-bearing minerals in the subducting slab [e.g., Poli and Schmidt, 2002; Wallace, 2005; Pyle and Mather, 2009; Baker and Balcone-Boissard, 2009]. The abundance of chlorine in typical arc-related rhyolite melts may reach 0.85 wt% (although more typically ranges up to around 0.45 wt%) [Wallace, 2005]. The concentration of bromine in rhyolitic melts has been reported in the range 0.0001–0.03 wt%, based on published melt inclusion and matrix glass data [Aiuppa et al., 2009; see also Gerlach, 2004; Aiuppa et al., 2005; Bureau et al., 2010;

Table 1. Halogen and Sulfur Gas Ratios From the Literature, Measured Spectroscopically (Either by FTIR for HCl/SO₂, or by DOAS)^a

Volcano	Magma Composition	Tectonic Setting	Date of Measurement	HCl/SO ₂ (mol/mol)	BrO/SO ₂ (mol/mol)	OCIO/SO ₂ (mol/mol)	References
Ambrym	Basalt	Subduction zone	Jan 2005 Mar 2005 Jul 2005 Aug 2007		$2.3\text{--}4.1 \times 10^{-4}$ 1.4×10^{-5} 5.4×10^{-5} $4.5\text{--}7.0 \times 10^{-4}$	N/A	<i>Bani et al.</i> [2009]
Erebus	Phonolite	Rift	Dec 2004 Dec 2005	0.5	2.5×10^{-4}	N/A	<i>Oppenheimer and Kyle</i> [2008] <i>Boichu et al.</i> [2011]
Etna	Basalt	Subduction related	Jul 2001 May 2005 Sept 2003 Aug 2008 Aug 2004 2004–2008 May 2010	0.3 (summit) 0.5	2.6×10^{-4} 4.7×10^{-4} 2.1×10^{-4} 2.1×10^{-4} $1.1\text{--}2.4 \times 10^{-4}$ 1.3×10^{-4}	5.7×10^{-5}	<i>Burton et al.</i> [2003] <i>Louban et al.</i> [2009] <i>Allard et al.</i> [2005] <i>Bobrowski and Platt</i> [2007] <i>Bobrowski and Platt</i> [2007] <i>Bobrowski et al.</i> [2007] <i>Bobrowski and Giuffrida</i> [2012] <i>Heue et al.</i> [2011]
Eyjafjallajökull	Dacite mixed with basalt	Mantle plume	May 2010				
Masaya	Basalt	Subduction zone	Mar 1999 May 2001 Mar 2003 Apr 2007	0.5 0.25	8.0×10^{-5} 3.0×10^{-5}	N/A	<i>Horrocks et al.</i> [1999] <i>Duffell et al.</i> [2003] <i>Bobrowski and Platt</i> [2007] <i>Kern et al.</i> [2009]
Popocatepetl	Andesite	Subduction zone	Nov 2008	0.6 (passive)	3.0×10^{-5}	N/A	<i>Stremme et al.</i> [2011] <i>Boichu et al.</i> [2011]
Redoubt	Andesite	Subduction zone	Aug 2010		1.0×10^{-4}	N/A	<i>Kelly et al.</i> [2013]
Sakurajima	Basalt to andesite	Subduction zone	May 2004	0.32	1.0×10^{-3}	N/A	<i>Lee et al.</i> [2005] <i>Mori and Notsu</i> [2003]
Soufrière Hills	Andesite/basaltic andesite	Subduction zone	May 2002 Oct 1999 – Oct 2000 Apr 2011 Apr 2002 Sept 2004	0.5 0.3–12 0.5 1.0	1.0×10^{-3} 1.0×10^{-4} 2.1×10^{-4}	N/A 5.0×10^{-4} N/A	<i>Bobrowski et al.</i> [2003] <i>Villemant et al.</i> [2008] <i>Edmonds et al.</i> [2002] <i>SAC</i> (2011) This study <i>Burton et al.</i> [2007]
Stromboli	Basalt	Subduction zone	Sept 2004				
Villarica	Basaltic andesite	Subduction zone	Mar 2009 Nov 2004	0.3	1.3×10^{-4}	N/A	<i>Sawyer et al.</i> [2011] <i>Bobrowski and Platt</i> [2007]

^a“Passive” denotes studies where a distinction was made between explosive release of gas and quiescent degassing. All HCl/SO₂ ratios have been recalculated to molecular ratios where necessary. Where the volcano was not erupting at the time that the gas measurements were made, magma composition is taken as that of the most recent eruption prior to the measurements.

Kutterolf et al., 2013]. The SHV is notable in comparison to other arc volcanoes for the relative chlorine enrichment observed in its gas emissions, in apatite and in melt inclusions [*Edmonds et al.*, 2002; *Oppenheimer et al.*, 2002; *Villemant et al.*, 2008; *Humphreys et al.*, 2009]. It has been inferred that volatiles in the atmospheric plume are sourced from both the mafic magma at depth and from andesite degassing during decompression and eruption [*Edmonds et al.*, 2001].

Plagioclase-hosted melt inclusions in SHV lavas contain up to 0.45 wt% chlorine [*Edmonds et al.*, 2001; *Humphreys et al.*, 2009]; the concentration of bromine in melt inclusions has not been measured. *Signorelli and Carroll* [2001] determined experimentally that the SHV magma could contain up to 0.68 wt% Cl before an immiscible brine phase would form. The exsolution of chlorine from melt takes place via partitioning into an aqueous phase, which depends primarily on melt composition [*Webster* 1992; *Webster et al.*, 1999; *Shinohara et al.*, 1989; *Shinohara*, 1994]. A fraction of the chlorine degassing from the rhyolitic melt likely also occurs at magma reservoir pressures, and may be controlled by the activity of H₂O in the coexisting vapor. Zonation in the Cl/OH content of hornblende phenocrysts may be explained by the addition to the andesite of a hot CO₂-rich vapor from basaltic magma, thereby changing the activity of H₂O and Cl partitioning behavior [*Humphreys et al.*, 2009]. The mass flux of chlorine-bearing gases is dependent on the degassing flux of water and on crystallization, which will drive Cl out of the melt during degassing-induced undercooling [*Villemant and Boudon*, 1999; *Edmonds et al.*, 2002; *Villemant et al.*, 2005, 2008]. This mechanism for chlorine degassing provides an explanation for high HCl/SO₂ ratios in the volcanic gases during lava extrusion, when chlorine is actively partitioning into the vapor exsolved on magma ascent, promoted by rapid crystallization of microlites in the rhyolitic melt. Changes in the ratio of sulfur to chlorine in volcanic gases may also be caused by second boiling during prolonged cooling and crystallization of shallow-emplaced or erupted magmas [*Symonds et al.*, 1996]. Very little is understood, in contrast, about the behavior of bromine during degassing.

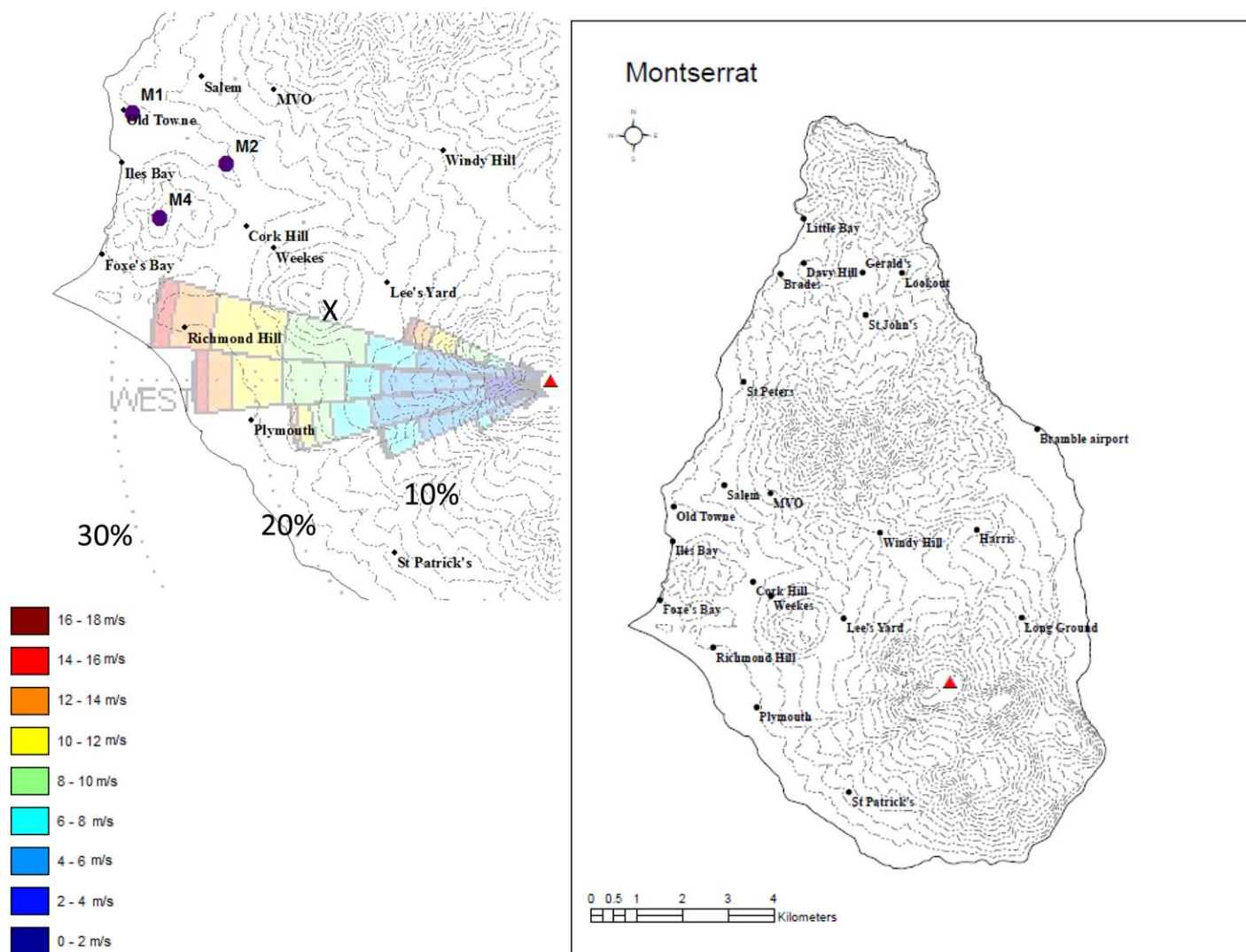


Figure 1. Map of Montserrat with an inset showing the wind speeds (m/s) and directions during the fieldwork period. M1–M4 are the measurement sites. Angles on the wind rose are 20°, and color indicates the wind speed. Length of section corresponds to the % of time that the wind took the specified direction and speed. Contours are 500 m.

In 2002, the bromine monoxide (BrO) content of a volcanic plume was measured for the first time using a miniature ultraviolet spectrometer at SHV [Bobrowski *et al.*, 2003]. These were the first observations of reactive bromine associated with volcanic degassing, and they were made during a period of eruption. BrO is thought to form from magmatic hydrogen bromide (HBr) via two mechanisms. In the very early plume, HBr can react with OH radicals to form Br [Roberts *et al.*, 2009]. Alternatively and more prominently, HBr can react with HOBr on aerosol particles to form Br₂, which photolyses to Br [von Glasow, 2010]. Br then reacts with ozone (O₃) to form BrO. It has been observed at a number of volcanoes (Table 1), but not previously interpreted with respect to bromine partitioning at depth. The abundance of BrO relative to SO₂ has been observed to increase rapidly in the first few minutes after release from the vent [Bobrowski *et al.*, 2007]. The ratio has also been shown to vary with volcanic activity at Etna [Bobrowski and Giuffrida, 2012]. However, the behavior of bromine in melts is very poorly understood. Under experimental conditions, synthetic melts suggest a higher fluid-melt partition coefficient for Br than for Cl [Bureau *et al.*, 2000]. However, Villemant *et al.* [2008], based on studies of SHV, posit that the ratio of fluid-melt partition coefficients is closer to 1. Recent experiments by Louvel [2011] demonstrate that, at upper crustal pressures, there is still considerable uncertainty regarding bromine behavior, and this is further demonstrated in the data presented by Kutterolf *et al.* [2013]. There are thus outstanding questions concerning the partitioning behavior of Br between melt

and hydrous vapor in relation to that of Cl. There are also resulting questions concerning the potential use of BrO as a monitoring tool [Bobrowski and Giuffrida, 2012].

In 2011, a series of spectra were acquired at SHV using a UV spectrometer and analyzed by DOAS in order to quantify the relative abundances of SO₂, BrO and any other reactive gas species. Our principal aim was to identify whether or not BrO was still being generated in the plume during a quiescent period, i.e., during an interval of no lava dome growth when we might expect the proportion of halogens to be reduced. The relative abundances of Cl and Br, given our understanding of the degassing budget at SHV, might yield insight into the degassing behavior of these volatiles from the andesite. Our findings have implications for the utility of measuring BrO/SO₂ for volcano monitoring purposes. Given the high levels of halogens recorded at SHV by previous authors [Bobrowski *et al.*, 2003; Edmonds *et al.*, 2001, 2002; Christopher *et al.*, 2010], we also analyzed spectra for the presence of OCIO and report for the first time measurements of this species at SHV, which has important implications for understanding reactive halogen chemistry in volcanic plumes.

2. Methods

2.1. Measurements

Measurements were made on seven days over three weeks during April 2011, on days when conditions were close to optimal for minimizing the impact of scattering effects on DOAS retrieval results (see “Field conditions” below). Field locations are shown in Figure 1. Efforts were made to estimate the evolution of the plume chemistry with distance from the vent. The measurement locations varied depending on meteorological conditions and plume direction. While the dominant plume direction on Montserrat is to the west, over the former capital city Plymouth, on several of our measurement days the plume was transported to the west-north-west.

An Ocean Optics 2000+ UV spectrometer attached to a single lens telescope via a solar-resistant optical fibre bundle and assembled in a thermostabilized box was used. The resulting field of view was 8 mrad. The spectrometer acquires spectra with a wavelength range of 285–430 nm and a resolution of 0.47 nm (full-width-at-half-maximum), which excludes under-sampling effects [Roscoe *et al.*, 1996; Chance *et al.*, 2005]. A Hoya U-330 ultraviolet filter was placed in front of the lens to reduce the amount of stray light in the spectrometer. The device was mounted on a tripod. Wavelength calibration and instrumental function of the spectrometer were determined by means of mercury and cadmium calibration lamps. These results were tested using the calibration approach of QDOAS [Danckaert *et al.*, 2012]. The solar spectrum reported by Chance and Kurucz [2010], convolved to spectrometer’s resolution, was compared with spectra measured outside the plume.

Spectra were recorded using Ocean Optics Spectrasuite software and DOASIS [Kraus, 2006]. The telescope elevation was fixed so as to point at the plume centre, as judged visually. The angle of elevation varied from day to day between 15° and 45°. The azimuth of the observation direction varied depending on the desired plume age. Total integration time (exposure time multiplied by the number of coadded spectra acquired) for the individual measurements was maintained at 10 s, and the exposure time varied automatically depending on the light conditions in order to avoid saturation effects. Plume-free background spectra were measured before and after every measurement period. The background spectra were recorded at comparable elevation angles and azimuths to the measurements, usually above the plume, toward the zenith and also toward the north. Background spectra were examined in the field to check that they were registered outside of the plume. This involved retrieval of SO₂, ozone and fitting of the Ring effect, but with the convolved solar spectrum used as a reference [Salerno *et al.*, 2009]. In addition, dark (10 s integration time without coadds) and offset (3 ms integration time 10,000 coadds) spectra were recorded before and after every measurement period.

2.2. Field Conditions

Montserrat is subject to strong easterly winds, which dispersed the plume rapidly off the island on most of the measurement days, such that the plume transport was turbulent rather than laminar. The plume was largely transparent, but varied in opacity. Measurements were performed only when plume transmittance was ≤ 0.75 (estimated by using background and plume spectra at 370 nm) and horizontal visibility was at least 20 km. The plume width at locations where spectra were collected was about 2 km (based on airborne traverses performed during 2012). Thus the extinction of plume aerosols is less than 0.14 km^{-1} whilst the

Table 2. Summary of Data Sets Collected During the Measurement Period^a

Data Set	Date in Apr 2011	Telescope Elevation (°)	Telescope Azimuth (°)	Wind Speed (Standard Deviation) (Average m/s)	Wind Direction (Standard Deviation) (°)	Approximate Plume Age (min)	Approx distance to plume centre (km)	No. Spectra before average	Local Start Time	Local End Time
2M1B	2	18	240	11.8 (2.1)	99.2 (9.4)	18	4	410	12:40	15:08
2M2A	2	23	150	11.4 (1.5)	98.5 (7.2)	5	3	110	16:10	16:45
3M1C	3	28	120	10.4 (1.3)	94.3 (8.3)	4	5	153	15:34	16:23
9M1A	9	45	185	11.0 (1.5)	99.9 (8.8)	11	3	221	12:08	13:22
9M4A	9	20	165	10.3 (1.3)	101.1 (8.2)	8	2	250	15:54	17:09
10M1A	10	25	150	8.2 (1.2)	98.9 (9.2)	11	4	165	13:26	14:20
10M4A	10	20	195	8.4 (1.1)	97.4 (8.0)	13	2	292	16:11	17:35
17M4A	17	15	230	4.5 (1.1)	77.5 (14.2)	60	12	202	13:05	14:15
17M4B	17	15	205	5.3 (1.1)	68.5 (10.6)	28	4	214	14:34	15:51
17M4C	17	20	170	5.7 (1.2)	73.4 (9.4)	14	3	201	16:11	17:38
18M4B	18	25	125	4.4 (0.8)	91.6 (9.4)	12	3	405	15:18	17:37
19M1A	19	30	130	3.5 (1.4)	88.5 (17.2)	12	5	263	11:18	12:50

^aSee Figure 1 for the location of the measurements, indicated M1–4 in the data set name (which takes the format, date-location set).

extinction of the background aerosols is about 0.20 km^{-1} . As a result the scattering effects on DOAS retrievals were expected to be relatively weak [Kern *et al.*, 2010] (see also “Data evaluation” below). Some cloud was always present (cloud cover about 2–4 oktas). Air temperature during measurements varied between 25 and 28°C. Relative humidity is assumed to be higher than 40% (long-term averages for Montserrat are recorded as around 75% in March to May). Bobrowski and Giuffrida [2012] found that relative humidity did not affect measurements at Etna, and according to the model of Oppenheimer *et al.* [2006a, 2006b] a high humidity of >40% should not affect HBr partitioning into the aqueous phase according to the information currently available. However, such effects cannot be ruled out, as measuring in-plume humidity was not possible and neither the measurements of Bobrowski and Giuffrida [2012] nor the model of Oppenheimer *et al.* [2006a, 2006b] apply to the exact conditions in the early plume on Montserrat.

Approximate plume age was calculated by dividing the distance of the measured light path from the volcano by the wind velocity. The measurements of wind speed and direction were obtained from the Montserrat Volcano Observatory (MVO) meteorological station on St George’s Hill (altitude 350 m a.s.l.). The station is close to the volcano and elevated over the places where plume has been observed (Figure 1). The terrain where the plume propagates is complex (small hills and deeply incised river beds) and thus some variations in the wind velocity at different heights are always present, i.e., some parts of the observed plume were older than others. Nevertheless, MVO consider wind data from meteorological station on St. George’s Hill representative for the plume dispersion and use them in calculating SO₂ fluxes [Edmonds *et al.*, 2003c; Christopher *et al.*, 2010]. The measurement positions, together with description of registration parameters, number of registered spectra during measuring period, wind data and corresponding estimates of plume age are summarized in Table 2.

2.3. Data Evaluation

A detailed description of the data evaluation procedures is given in the Appendix A (supporting information). Spectra were initially corrected for offset and dark current. They were added in groups of five to

improve the signal-to-noise ratio, and fitted in three fitting windows. The first fitting window spanned 310.78–323.67 nm, and included a background spectrum, a ring spectrum, and O₃ and SO₂ cross sections (see Table 3). Column densities for BrO and OCIO were retrieved in two windows: 331–357 nm [Kern *et al.*, 2009] and 320–360 nm [Bobrowski *et al.*, 2003, 2007]. Cross sections for O₃, O₄, SO₂, BrO, OCIO and NO₂ were included in the fit. An example fit is shown in Figure 2. All ratios are reported as molar ratios unless indicated otherwise.

Table 3. Absorption Cross Sections Used in the Fitting Process.

Gas	Reference Cross Section	Temperature/K
SO ₂	Bogumil <i>et al.</i> [2003] ^a	293
O ₃	Burrows <i>et al.</i> [1999]	273
O ₄	Greenblatt <i>et al.</i> [1990]	296
BrO	Fleischmann <i>et al.</i> [2004]	293
OCIO	Kromminga <i>et al.</i> [2003]	293
NO ₂	Vandaele <i>et al.</i> [1998]	293
HCHO	Meller and Moorgat [2000]	298

^aThe choice of cross section was made because Bogumil *et al.* [2003] measured temperature-dependent cross sections. Their data were collected at a resolution of 0.2nm using SCIAMACHY, and therefore we deconvolved the cross section to 0.1 nm for our retrievals.

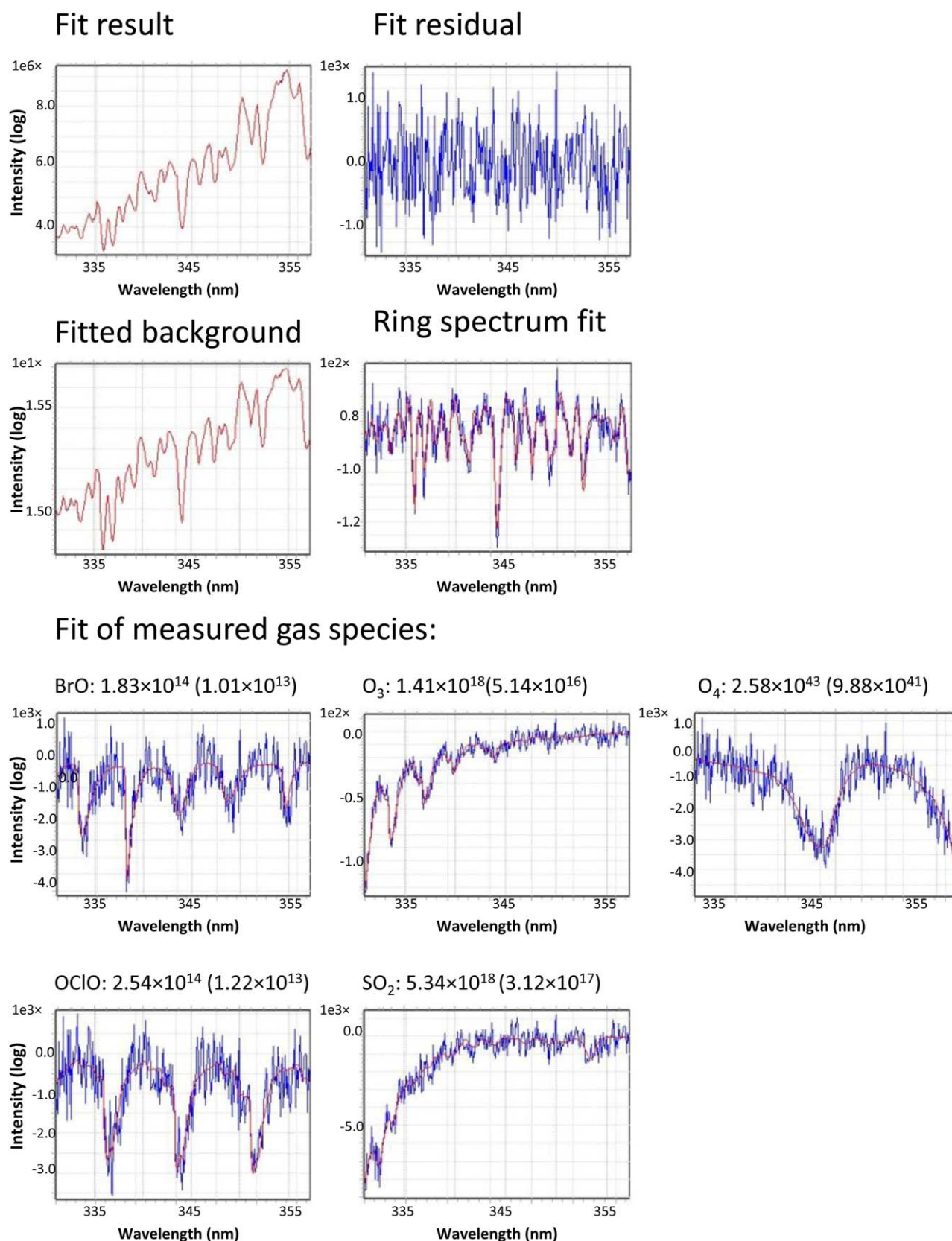


Figure 2. Example of a fit for BrO and OClO in the range 331–357 nm. Column amounts are stated for each gas, with error in brackets. Units are intensity (arbitrary units). All shifts < 0.2 in magnitude; squeeze = 1 except for SO₂ (0.985) and Ring (0.988).

Table 4. Summary of Data Sets Obtained, and the Detection of Reactive Halogens in the Plume^a

Data Set	Average SO ₂ CA × 10 ¹⁸ Molecules/cm ²	Average BrO/SO ₂ mol/mol × 10 ⁻⁴	Average OCIO/SO ₂ mol/mol × 10 ⁻⁴	Average BrO/OCIO mol/mol
2M1B	1.4	1.1	5.8	0.2
2M2A	3.1	1.0	n.d.	
3M1C	0.8	1.5	n.d.	
9M1A	0.6	2.6	d.l.	
9M4A	0.8	3.7	d.l.	
10M1A	1.4	1.8	d.l.	
10M4A	1.4	2.4	d.l.	
17M4A	0.4	2.0	n.d.	
17M4B	0.7	2.5	n.d.	
17M4C	0.4	2.5	n.d.	
18M4B	1.0	3.1	4.2	0.7
19M1A	0.9	1.3	5.2	0.2

^aThe abbreviation d.l. means that although the species was detected, it was very close to the detection limit. M1–M4 represent the location of the measurements, as shown in Figure 1. Times are local (equivalent to Eastern Standard Time, UTC–5 h). Plume age was calculated from the wind speed and distance of measured light path from the volcano.

3. Results

Table 4 shows the average column amounts of SO₂ retrieved in each of the data sets. We applied a detection limit of three times the retrieval error in selecting the data. This allows for small errors due to scattering and *I*₀ effects. Table 4 also shows average ratios obtained for each data set. All ratios are based on molar proportions. BrO/SO₂ was lowest (down to 5.0×10^{-5}) in young plume, with higher values ($>1.0 \times 10^{-4}$) occurring for plume ages exceeding 8 min, in general. However, after the first 20 min, there seems to be little impact of plume age on BrO/SO₂. This is consistent with results from other studies [e.g., Bobrowski and Giuffrida, 2012]. The BrO/SO₂ molar ratio was consistently around 2×10^{-4} for a plume of similar age to that measured by Bobrowski *et al.* [2003]. OCIO was identified conclusively in three of the data sets.

Figure 3 shows correlations between SO₂ and BrO for six of the measurement days. The BrO/SO₂ ratio is consistent across the period, though there is some variation in slant column densities.

The final week of measurements was characterized by lower wind speeds and clearer skies. Attempts to measure the ageing plume offshore on 17 April 2011 had limited success due to attenuation and the angle at which the measurements had to take place (over the ocean, with a long path through the plume). Successful measurements demonstrate that the ratio of BrO to SO₂ remained relatively constant through the different plume ages on 17 April (Figure 4a). On 9 and 10 April, higher ratios of BrO/SO₂ were found later in the day (Figure 4a; compare Table 3). There is no discernable relationship between SO₂ column amount and the BrO/SO₂ ratio (Figure 4b).

It was possible to detect both BrO and OCIO on 18 April (Figure 5). While the correlation between BrO and OCIO is relatively good, the relationship between SO₂ and OCIO is less so but still apparent. Note that correlation between SO₂ and OCIO is weaker than that between SO₂ and BrO. While OCIO was detected on 2 April, it was not present at sufficient levels for reliable retrievals during the second week of measurements (9–16 April). BrO abundance was lower relative to SO₂ in the first week of measurements, coincident with a higher SO₂ flux [MVO, 2011].

4. Discussion

4.1. Bromine in the Soufrière Hills Magmas

Our results suggest that the ratio of BrO/SO₂ was almost an order of magnitude lower at the time of our measurements compared with those of Bobrowski *et al.* [2003] (Figure 6). Measuring the plume during eruptive activity in May 2002, Bobrowski *et al.* [2003] obtained an average BrO/SO₂ ratio of 8.2×10^{-4} (and also quote 1.0×10^{-3} as representative), while our average ratio is 1.75×10^{-4} and our highest is 3.1×10^{-4} (Table 3 and Figure 3). While Bobrowski *et al.* [2003] measured slant column amounts (SCA) of BrO up to 2.0×10^{15} molecules cm⁻², our highest BrO SCA is 5.78×10^{14} molecules cm⁻². There are several possible explanations for this. Initially, we consider the possibility that the differences are within error of the measurement technique. We then examine two further possibilities – a change in the rate of HBr oxidation to

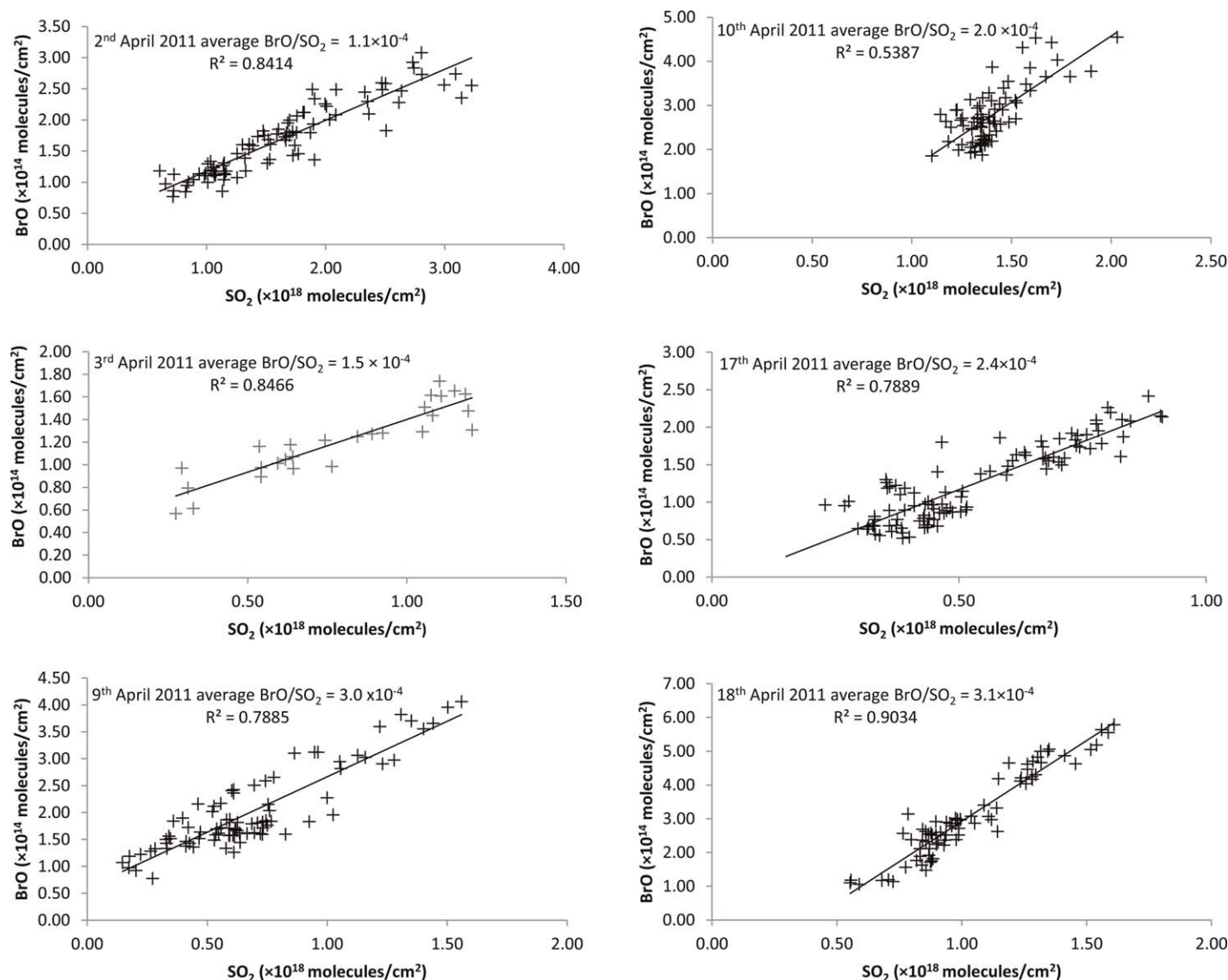


Figure 3. Results for BrO for several days during April 2011, including all data recorded on each day. Typical errors are 3×10^{13} molecules cm^{-2} for BrO and 2.5×10^{16} molecules cm^{-2} for SO₂; all data shown are above the detection limit of three times the retrieval error.

BrO (with the implication that the flux of bromine from the volcano might not have changed), and a change in the partitioning behavior of Br from the melt into the gas phase.

The DOAS technique and retrievals are subject to instrumental and analytical error. The instrumental setup for this project and the locations of the measurements were different to that of Bobrowski *et al.* [2003]. Bobrowski *et al.* [2003] and Bobrowski and Platt [2007] do not provide details about the meteorological conditions and transparency of the plume during their measurements. They also used a different wavelength range for the evaluation of SO₂ (307.5–316 nm), while we used 310–323.67 nm to improve the signal-to-noise ratio. It is possible, too, that the turbulence of the plume due to varying wind velocities could impact the results. However, our ratios are relatively constant in spite of significant variations in weather conditions within our measurement period.

The SO₂ flux at the time of the measurements by Bobrowski *et al.* [2003] was slightly lower than that during our measurements, which might imply that the changes in the ratio in part relate to SO₂ not BrO. Errors on the SO₂ measurements are also high (10–30%; Edmonds *et al.*, 2003a, 2003b; Christopher *et al.*, 2010).

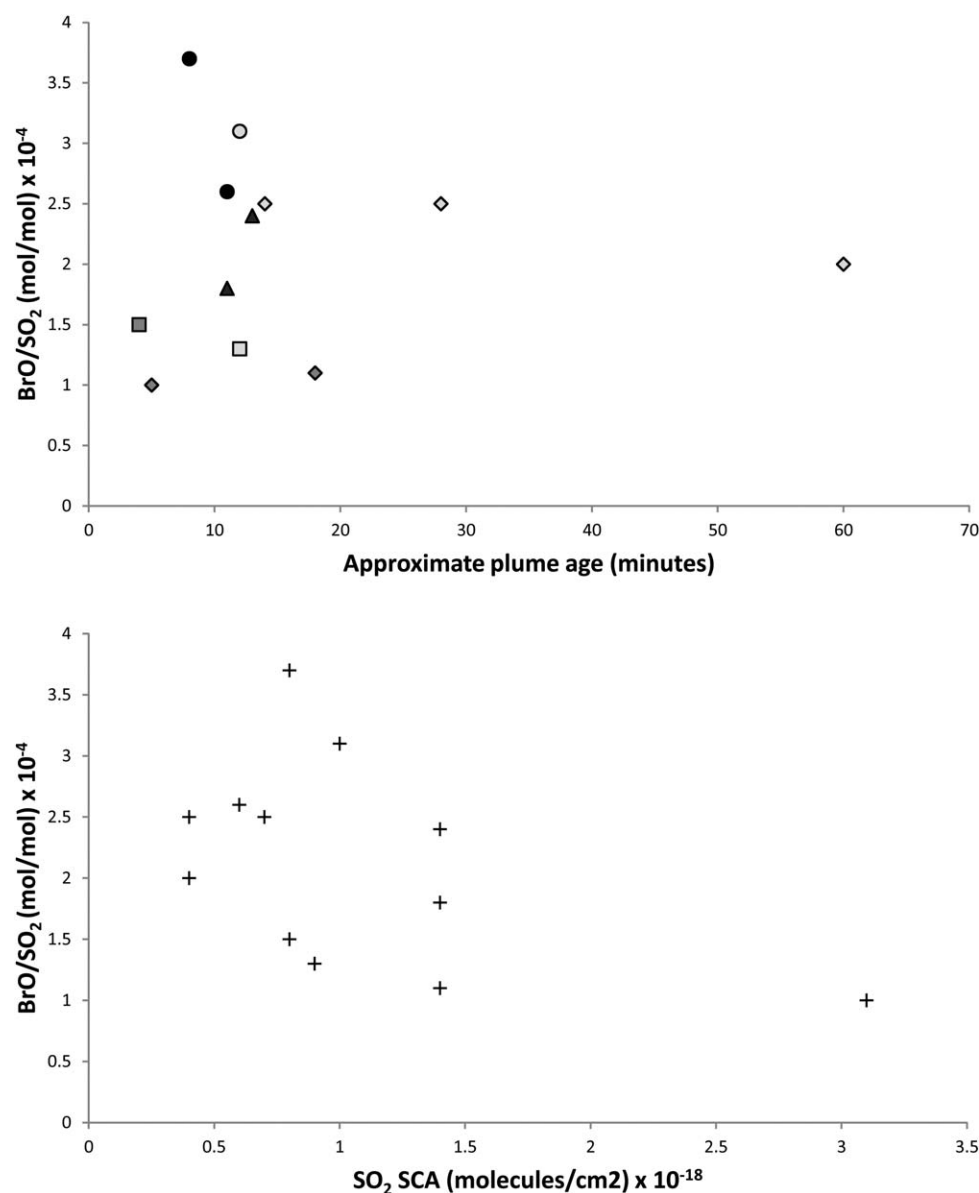


Figure 4. (a) Plume age against BrO/SO₂ ratio, color-coded by date. Gray diamonds: 2 April; gray square: 3 April; black circle: 9 April; black triangle: 10 April; light gray diamond: 17 April; light gray circle: 18 April; light gray square: 19 April. (b) SO₂ column amounts against BrO/SO₂ ratio.

However, the column amounts for SO₂ measured by Bobrowski *et al.* [2003] are comparable to ours (with the exception of the 2M2A data set on 2 April, which represents very young plume with a higher SCA of SO₂). We also obtain a lower ratio regardless of time of day and plume age, encompassing the possible ranges of measurements by Bobrowski *et al.* [2003] and therefore excluding the possibility of significant influence from processing artefacts. While Bobrowski *et al.* [2003] may have underestimated SO₂ due to saturation effects, this is not consistent with the lower flux and similar column amounts in 2002. Our observation that most of the change in BrO/SO₂ occurs in the first few minutes is consistent with the results of Bobrowski *et al.* [2007] and Bobrowski and Giuffrida [2012]. While some of the difference might be attributable to error, its magnitude is large enough that other mechanisms should be explored. Therefore, bearing in mind the changing volcanic activity, it is probable that there is less BrO relative to SO₂ (the flux of which remains relatively high and constant; Figure 7) in the plume at SHV during eruptive pauses. If the difference in measured BrO/SO₂ between periods of dome growth and hiatus is real, it suggests that, for our measurement period either (i) lower reaction rates to convert HBr to BrO in the plume or (ii) less HBr in the magmatic gas phase relative to SO₂. We will discuss these possibilities in turn.

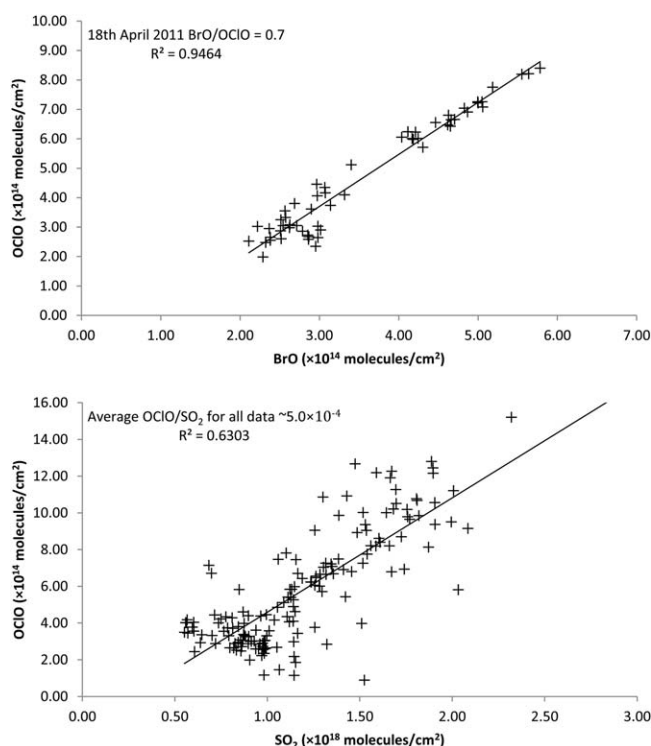


Figure 5. BrO versus OClO slant column amounts for 18 April 2011 and OClO versus SO₂ for all data. See caption of Figure 3 for information on formal errors for BrO and SO₂; typical error is 6×10^{13} molecules cm⁻² for OClO; all data shown are above the detection limit of three times the retrieval error.

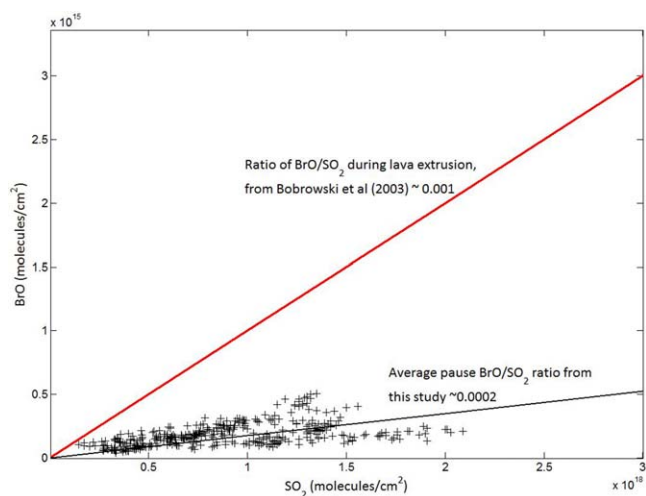


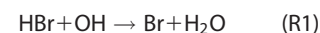
Figure 6. All BrO versus SO₂ SCA measurements. Bold red line shows the average BrO/SO₂ of Bobrowski et al. [2003]. Black line shows the average from our measurements, shown in black.

and SO₂ data to calculate the potential difference in oxidation rates.

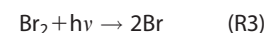
Bobrowski et al. [2003] measured the plume in May 2002; our measurements were carried out in April 2011. It is unlikely that seasonal variation in actinic flux affected the difference in measurements [e.g., Madronich, 1987; Dlugokencky et al. 1996]. Our measurements spanned a 3 week period, and were made at a range of times of day. The volcanic plume may have been smaller during our measurements and was potentially

4.1.1. Plume Processes: Reaction Rates for HBr to BrO

In this section, we assume, as is well documented [e.g., Gerlach, 2004; Oppenheimer et al., 2006a; Bobrowski et al., 2007; Roberts et al., 2009], that BrO is not a primary magmatic gas. The formation of BrO in volcanic plumes via conversion of HBr initially occurs due to reaction with OH radicals:



This reaction occurs in the earliest plume. Reaction of BrO with HO₂ and NO₂ may then occur [but see von Glasow, 2010], generating HOBr and BrONO₂. These are highly reactive in acidic aerosols [Oppenheimer et al., 2006a, 2006b], generating BrCl and Br₂—with Br₂ being favored under volcanic conditions [Roberts et al., 2009]. This reaction rapidly increases the Br₂ abundance in the plume. Br₂ preferentially partitions back into the gas phase, and it is rapidly photolysed:



Br then reacts with ozone (R2). The rapid acceleration of BrO formation in the early volcanic plume is well documented by both observations and models [Bobrowski and Platt, 2007; Oppenheimer et al., 2006a, 2006b; Bobrowski and Giuffrida, 2012; Bobrowski et al., 2007; Afe et al., 2004]. It is dependent on the availability of OH, O₃ and aerosols – and on the mixing ratio of atmospheric and volcanic gas [Martin et al., 2006]. The availability of photons for reaction with Br₂ is clearly also important. This could vary seasonally, with time of day and with cloud cover. Initially we will discuss variability in environmental factors, and then use HCl

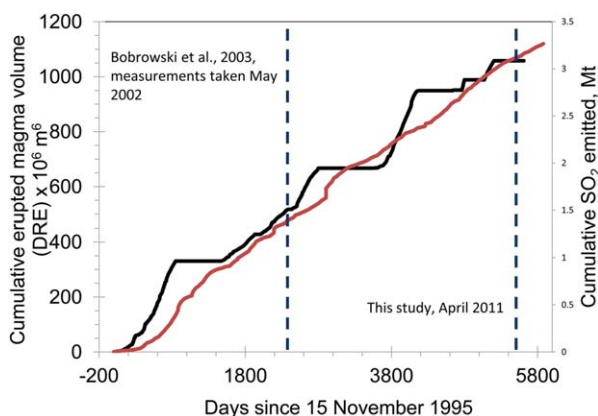


Figure 7. Cumulative SO_2 emission at the Soufrière Hills (red) in relation to volume of lava extruded (black) and the timing of the measurements of this study and that of Bobrowski *et al.* [2003]. Data for lava volume from Wadge *et al.* [2014].

more transparent due to a lack of ash/condensation, both of which should facilitate, not inhibit, BrO formation (by promoting both mixing with ambient air and photolysis).

At the time of the measurements, fumarole temperatures on the lava dome measured remotely by MVO exceeded 500°C [MVO, 2011]. This suggests that temperatures in the shallow system were close to magmatic and that there has been little change in gas temperature that might affect HBr reactions [Gerlach, 2004; Martin *et al.*, 2006, 2012; Roberts *et al.*, 2009]. However, other factors in the plume may still contribute

to changing rates of conversion of HBr to BrO (e.g. atmospheric effects and aerosol processes; see for example Martin *et al.*, 2012), and we investigate this further using published data from petrological studies of SHV.

Pumiceous clasts with high vesicularity at SHV have higher Cl and Br content than dome rocks, and both species appear to have similar degassing behaviors [Villemant *et al.*, 2008] (using whole-rock Br content corrected for the small amount in hornblende phenocrysts). Open-system degassing promotes halogen exsolution. Both species have fluid-melt partition coefficients >1 in water-rich systems [Villemant *et al.*, 2008; Bureau *et al.*, 2000]. Halogens are enriched in the melt by crystallization whilst also being depleted due to H_2O degassing and partitioning into the gas phase. While experimental data from Bureau *et al.* [2000] suggest that gas-melt partition coefficients between the halogens increase from Cl to Br, these data are based on synthetic albitic melts. The modeling of Villemant *et al.* [2008] suggests that the halogens (other than F) in fact have similar vapor-melt partition coefficients in natural systems. They further report that the Cl/Br ratio in the SHV andesite is anomalously low (of the order of 160 by mass) and suggest that this relates to shallow contamination of the melt. The Cl/Br mass ratio in the basalt, on the other hand, is ~ 300 [Villemant *et al.*, 2008].

The mass ratio of Cl in HCl gas to Br in BrO (Cl/Br^*) has been estimated as ~ 500 [Villemant *et al.*, 2008], based on measurements obtained via infrared and ultraviolet spectroscopy of the plume [Oppenheimer *et al.*, 1998; Bobrowski *et al.*, 2003; Edmonds *et al.*, 2002]. The inferred high rate of oxidation of HBr to BrO is contrasted with an inferred scavenging of Cl into aerosols and particulate surfaces, as suggested by leachate [Edmonds *et al.*, 2003a, 2003b] and aerosol data [Allen *et al.*, 2000]. Using the data obtained in all our measurements with an estimated SO_2 flux and HCl/SO_2 ratio (see Table 5), we obtain a Cl/Br^* mass ratio of 1300 ± 500 . This suggests that not only has BrO/SO_2 decreased but that BrO has decreased relative to HCl.

Following Villemant *et al.* [2008] and taking the ratio of the fluid-melt partition coefficients as unity, the mass of bromine in the fluid phase can be calculated from the mass of chlorine (based on the HCl/SO_2 mass ratio and an estimated SO_2 flux) and the concentration of both elements in the melt ($\text{Cl}/\text{Br} = 160$). This suggests that for 175 Mg of chlorine in the gas phase, there are 1.09 Mg of bromine (Br_{tot}). We would thus expect a BrO/SO_2 mass ratio of 7.3×10^{-4} for andesite degassing and 3.8×10^{-4} for basalt degassing—if all the bromine and chlorine in the melt is degassed in an open system and a third of the Br is oxidized to BrO. Our average BrO/SO_2 mass ratio is 3.2×10^{-4} . This suggests either that the ratio of the partition coefficients is not unity in our case, or that the amount of HBr being oxidized is lower than at the time of the measurements made by Bobrowski *et al.* [2003]. If the latter is the case, then we calculate that $\sim 15\%$ of the total bromine emission from the volcano was being oxidized during our measurement period. This is roughly half the mass of HBr that was being oxidized during the 2002 measurements.

4.1.2. Magma Processes: Changes in the Relative Partitioning of Halogens

Another plausible scenario based on the evidence presented here is that the HBr/SO_2 ratio of gas emitted from the volcano is lower during times of eruptive hiatus. This has implications both for Br partitioning

Table 5. Pertinent Quantities From the Literature, used in the Modeling^a

Parameter	Value	Data Source
SO ₂ flux average wk 1	696 tonnes per day	MVO Weekly Reports
SO ₂ flux average wk 2	514 tonnes per day	MVO Weekly Reports
SO ₂ flux average wk 3	596 tonnes per day	MVO Weekly Reports
SO ₂ flux during measurements of <i>Bobrowski et al.</i> [2003]	400 tonnes per day	<i>Villemant et al.</i> [2008]
Cl in melt inclusions	1500–4500 ppm	<i>Humphreys et al.</i> [2009]
HCl/SO ₂ mass ratio during measurements	0.3 ± 0.06	SAC Report 16, Appendix 2 [SAC, 2011]
HCl/SO ₂ mass ratio in measurements of <i>Bobrowski et al.</i> [2003]	0.5 ± 0.1	<i>Villemant et al.</i> [2008]
Cl/Br mass ratio (andesite)	160	<i>Villemant et al.</i> [2008]
Cl/Br mass ratio (basalt)	300	<i>Villemant et al.</i> [2008]
D _{Cl} /D _{Br} (experimental)	0.46	<i>Bureau et al.</i> [2000]
D _{Cl} /D _{Br} (modeled)	1	<i>Villemant et al.</i> [2008]

^aPartition coefficients from *Bureau et al.* [2000] are for their experimental conditions at 200 MPa, 900°C.

between fluid and melt, and also potentially for volcano monitoring. If the rate of atmospheric oxidation of HBr to BrO is the same for our observation period as for that of *Bobrowski et al.* [2003], then the Br emission relative to Cl and SO₂ has decreased. Bromine may be more “soluble” than sulfur in basaltic magmas at Mount Etna [*Bobrowski and Giuffrida*, 2012]. However, there are several critical differences between Etna and SHV that might affect bromine degassing. It is known that Cl partitioning, for example, is affected by pressure, temperature and composition of the melt and vapor phases [*Webster*, 1992; *Metrich and Rutherford*, 1992; *Bureau and Metrich*, 2003; *Louvel*, 2011], and is inhibited during closed-relative to open-system degassing [*Villemant et al.*, 2008]. Bromine may have a higher partitioning coefficient than chlorine in synthetic albitic melts [*Bureau et al.*, 2000], but this may not apply at SHV because of the lower polymerization of natural rhyolitic melts [*Villemant et al.*, 2008; *Balcone-Boissard et al.*, 2010; *Louvel*, 2011]; there are unresolved questions about the partitioning behavior of the halogens relative to each other in diverse systems. In this section, we speculate on a possible interpretation of our data in combination with measurements from Montserrat reported by the MVO, the work of *Bobrowski et al.* [2003] and that of *Villemant et al.* [2008], and compare this with results from the experimental petrology literature.

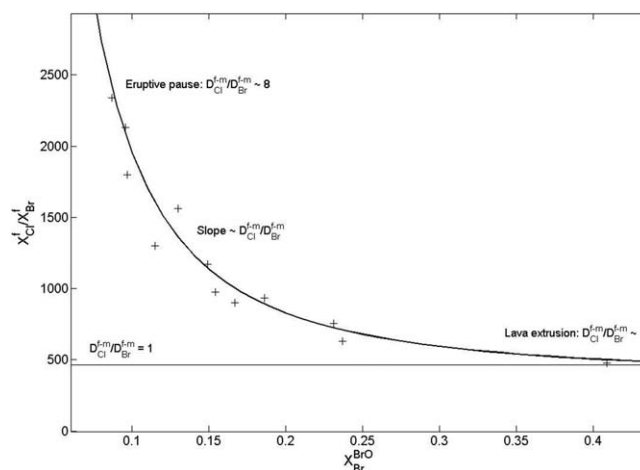


Figure 8. Best-fit model for the ratio between Cl and Br in the gas phase relative to Br in BrO. The data points represent our measurements and those of *Bobrowski et al.* [2003]. In this model, we use their average ratio of 8.2×10^{-4} . X_{Cl}^g / X_{Br}^g is calculated from the relevant HCl/SO₂ and BrO/SO₂ mass ratios and is the molar ratio between Cl and Br in the fluid phase (Cl in HCl, Br in HBr). Following *Villemant et al.* [2008], Br in HBr, X_{Br}^{HBr} , is assumed to be $3 \times Br^*$ (Br in BrO, X_{Br}^{BrO}). From the curve, we obtain an equation for X_{Cl}^g / X_{Br}^g , which we use to model the ratio of partition coefficients.

The decrease of Br relative to Cl suggests that the relative partitioning of Cl and Br into the fluid phase has changed. If we take the SO₂ fluxes reported by MVO during the period (Table 5), the relatively constant mass ratio of HCl/SO₂ of 0.3 ± 0.06 and our own mass ratios calculated from Table 4, this relationship can be modeled. Figure 8 shows a plot of Cl/Br in the gas phase (HCl and BrO) against the Br in BrO for our data and those of *Bobrowski et al.* [2003]. This suggests a power law upon which the ratio of partition coefficients may depend.

The partition coefficient of chlorine in rhyolitic melts varies with melt chlorine content [*Villemant et al.*, 2008]. Figure 8 suggests that the ratio between the fluid-melt

Table 6. Partition Coefficients for Br From Recent Studies at Magmatic Pressures^a

Source	Temperature (°C)	Pressure (MPa)	Composition	H ₂ O (wt%)	Av. D _{Br}	Av. D _{Cl}
Bureau <i>et al.</i> [2000]	900	200	Albite	2–3	17.5	8
Villemant and Boudon [1999]	900	200	Modeled in rhyolite	1–3	3.7 ± 1	10 ± 1.5
Louvel [2011]	800	200	Haplogranite-H ₂ O	2.4 ± 0.5	6.63	n.d.

^aCl partitioning was also measured; this is given for comparison.

partition coefficients for Cl and Br, $D_{Cl}^{f-m}/D_{Br}^{f-m}$, varies with gas Br content. We can quantify this relationship using the following equation:

$$D_{Cl}^{f-m}/D_{Br}^{f-m} = \left(X_{Br}^m/X_{Cl}^m \right) \left(X_{Cl}^f/X_{Br}^f \right)$$

In this equation, D represents the fluid-melt partition coefficients and X the concentrations in fluid and melt. This assumes that the original mass ratio of Cl/Br in the melt was 160 [Villemant *et al.*, 2008] (all Br being sourced from the andesite). From Figure 8, we obtain the relationship $X_{Cl}^f/X_{Br}^f = 19(Br^*)^{-1.8} + 285$. This gives a ratio of partition coefficients of $\sim 0.05(Br^*)^{-1.8} + 0.8$, suggesting that the ratio of partition coefficients, $D_{Cl}^{f-m}/D_{Br}^{f-m}$, ranges from 1 for Bobrowski *et al.* [2003] to 8 for our lowest BrO/SO₂ ratio in the entire data set, and 5 for the lowest average ratio: it is lower during eruptive activity. The ratio of ~ 1 suggested by Villemant *et al.* [2008] is an asymptote on Figure 8 and is therefore more likely to be achieved during eruptive activity. This may be due to changes in the magmatic system when fresh magma is not being supplied to shallow depths. This result may aid the reconciliation of the differing values of $D_{Cl}^{f-m}/D_{Br}^{f-m}$ so far provided in the literature (Table 6). We suggest, therefore, that while some HBr can exsolve from the melt at depth, the primary source of the previously recorded high Br emission at SHV is shallow and dependent upon eruptive activity. A sudden increase in BrO/SO₂ might therefore be a sensitive indicator of impending renewed activity. However, further work is necessary to constrain possible variations in HBr oxidation rate and the magnitude of errors associated with plume dispersion, aerosol processes and spectroscopic methods. This would enable assessment of the relative contributions of these factors in determining BrO/SO₂ ratios.

The reasons for a decrease in the ratio of partition coefficients may relate to degassing processes in the shallow magmatic system. HCl degassing is strongly coupled with melt water content, whereas this relationship has not been investigated for HBr. It is possible that the relative importance of the basaltic magma source compared to the andesite also shifts during pauses. It has been shown that the partitioning of Br and Cl in silicic melts varies with pressure [e.g., Bureau *et al.*, 2000; Louvel, 2011; Bureau and Metrich, 2003], and thus while at shallow pressures $D_{Br} > D_{Cl}$, this relationship may be reversed at higher pressures. Therefore, our results might indicate that there is no magma in the shallow system; HCl is lower in pauses because it is degassing at depth, and HBr is lower still because the Br partition coefficient at magma chamber pressures is lower than that of Cl. This is consistent with recent studies by Louvel [2011], which showed a decrease in Br partitioning with increasing temperature. Additionally, there are indications from the experimental literature that the use of synthetic melts rich in Na may not be appropriate in simulating magmatic conditions [Louvel, 2011; Villemant *et al.*, 2008; Baker and Alletti, 2012]. This strongly suggests the need for additional experimental research into the behavior of Br relative to H₂O and other halogens in natural melts under magmatic conditions.

4.2. OCIO in the Volcanic Plume

Volcanic plumes are chemically reactive, due both to the presence of a large range of compounds and to the availability of surfaces (ash and nonsilicate aerosol) on which reactions can occur [Mather *et al.*, 2003]. The abundance of thermal energy close to the vent, the humidity of the plume, the sudden exposure of a comparatively reduced magmatic gas mixture to atmospheric oxygen, and the incidence of sunlight also enhance its reactivity. Recent studies have reported detection of several reactive halogen oxides in volcanic plumes—BrO, OCIO and ClO [Bobrowski *et al.*, 2003, 2007; Kern *et al.*, 2009, 2010; Lee *et al.*, 2005; Sawyer *et al.*, 2011; Salerno *et al.*, 2009; Theys *et al.*, 2014]. Models and calculations suggest that these are not primary magmatic gases, but are produced in the plume due to aqueous phase oxidation of hydrogen halides

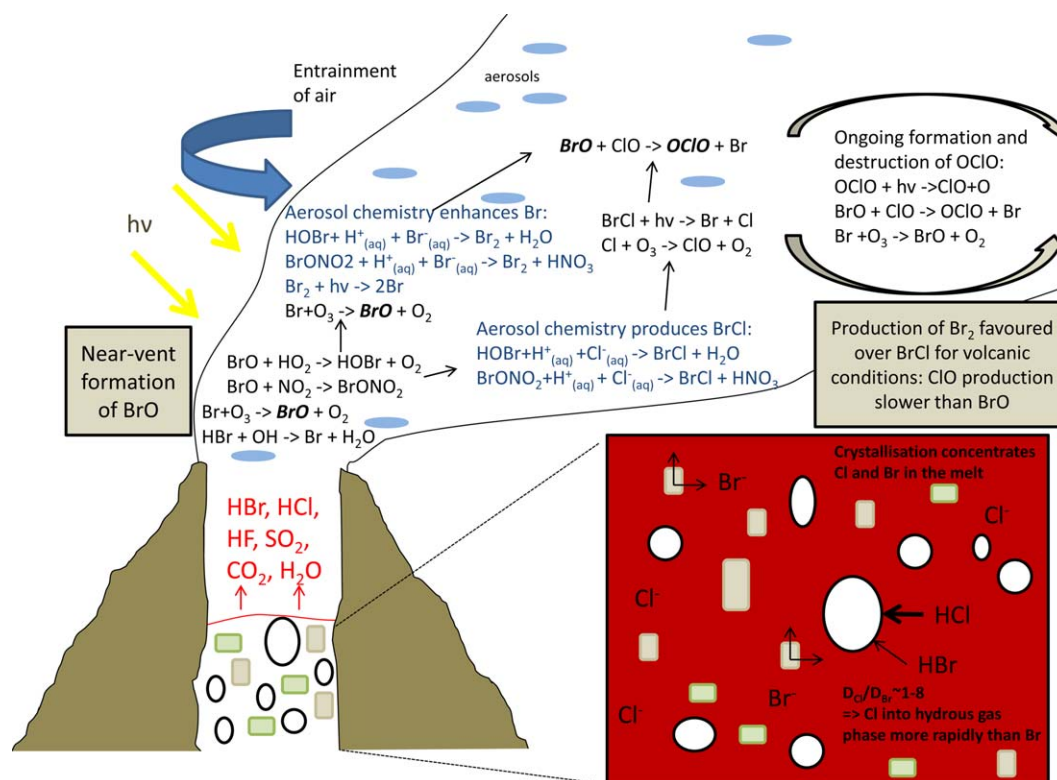


Figure 9. Summary conceptual model for the processes in the shallow system and the early plume at Soufrière Hills. Primary magmatic gas emissions are shown in red; aerosol-dependent reactions are shown in blue; other reactions are shown in black.

and subsequent photolysis of BrCl and Br₂ [Oppenheimer *et al.*, 2006a, 2006b; Bobrowski *et al.*, 2007; Gerlach, 2004; Aiuppa *et al.*, 2005; Roberts *et al.*, 2009]. This has been corroborated by observations that the abundance of BrO in the plume increases with distance from the vent [Bobrowski *et al.*, 2007; Oppenheimer *et al.*, 2006a, 2006b]. As BrO formation in volcanic plumes occurs as a result of the photodissociation of Br₂ followed by reaction with ozone, it has been observed to reach a maximum at midday [Kern *et al.*, 2009]. However, this was not clear in our data, with some of the later afternoon measurements being higher – this is consistent with models [e.g., von Glasow *et al.*, 2002]. BrO abundance has been observed to correlate with that of SO₂ during daylight [Bobrowski *et al.*, 2003; Kern *et al.*, 2009].

OCIO is formed from the reaction between ClO and BrO:



This reaction is therefore dependent on the formation of ClO, which is formed from photolysis of BrCl and reaction of Cl and ozone. While ClO has been reportedly detected in volcanic plumes [Lee *et al.*, 2005; Bobrowski *et al.*, 2007], the reliability of the measurements could be called into question because the ClO absorption in the ultraviolet coincides with that of SO₂ (which is typically very strong), and also due to the effects of stray light in the spectrometer in this wavelength interval [Kern, 2009]. ClO also reacts with NO₂ to form ClONO₂, which may then be hydrolyzed on sulfate aerosols to form HOCl and HNO₃, and HOCl photolyses to OH + Cl.

Two other reactions occur between BrO and ClO:



BrCl may also photodissociate to form Br and Cl. This ultimately increases the formation of BrO. Equation (R4) suggests that there should be a positive correlation between BrO and OCIO, and thus between SO₂ and OCIO. However, OCIO has a very short half-life in the atmosphere due to the following reaction:



OCIO formation also requires high levels of BrO and ClO in the plume. Since it can only be formed by the reaction of these two molecules, OCIO is a good indicator both of chlorine activation and of high BrO concentrations. OCIO concentrations in the atmosphere were observed to increase following the 1991 Pinatubo eruption, probably as a result of chlorine nitrate activation on aerosol surfaces [Solomon *et al.*, 1993].

Several factors affect halogen oxide formation [Gerlach, 2004; Wayne, 2000; Bobrowski *et al.*, 2007; Oppenheimer *et al.*, 2006a, 2006b; von Glasow *et al.*, 2009]. These include gas temperature (high temperature facilitates the direct release of Br and Cl from HBr and HCl); aerosol formation (which significantly increases the surface area for heterogeneous chemical reactions forming Br₂ and Cl₂) and acidity; time of day (due to the role of photolysis) and mixing between ambient air and the plume (since this facilitates the availability of ozone to form the halogen oxides).

In addition, OCIO detection was challenging because of some overlap between the BrO and OCIO cross sections and because of the relatively low column amounts of this gas on several days. OCIO was more challenging to retrieve in data sets collected during strong winds, or under conditions of substantial cloud cover (e.g., on 9 and 10 April). It also requires high levels of both ClO and BrO in order to form, suggesting that it might be sensitive to both halogen emission rates and to a stable plume with clear light path.

Using MVO's measurement of the HCl/SO₂ ratio in the gas phase (0.3 ± 0.06), we can also calculate the extent of HCl oxidation in the plume, if we assume that all OCIO in the plume is derived from HCl. Our OCIO/SO₂ ratios suggest that <0.01% of the total Cl in HCl in the plume was converted to OCIO. This is consistent with the complexity of chlorine reactions in the plume, and the instability of OCIO (estimated to have a half-life of around 9 s) [Kern, 2009]. It is likely that HCl remains the dominant Cl-phase in the plume for much longer than HBr [e.g., Kern, 2009; Bobrowski *et al.*, 2007], and much of the HCl may be scavenged by aerosols. In general, the correlation between SO₂ and OCIO was relatively poor. BrO and OCIO SCAs show a stronger correlation. This is expected, since OCIO formation is dependent on BrO and ClO. The high OCIO/SO₂ ratios during the day on 2 and 19 April 2011 are indicative of the highly dynamic environment of the tropospheric volcanic plume, the abundance of BrO and continuous formation of OCIO. Figure 9 summarizes the implications of the results from this study and those on which it builds.

5. Conclusions

BrO/SO₂ ratios at the Soufrière Hills Volcano on Montserrat decreased by almost an order of magnitude during an eruptive hiatus, and the ratio of Cl/Br in the gas phase increased. We suggest that this increase can be modeled by changes in the partitioning of these elements into the hydrous vapor phase in the absence of magma ascent. We suggest that the partitioning of the elements Cl and Br may vary relative to one another with degree of degassing. During magma ascent, vigorous water degassing and partitioning of halogens into vapor, the two halogen species partition into fluids to the same degree. At lower rates of degassing, however, when magma ascent and/or water degassing is sluggish, bromine degasses much less relative to chlorine. However, there are likely to be a number of factors affecting the difference in BrO/SO₂ ratios between phases of lava extrusion and eruptive pauses. Other possible causes include the quantity of Br in HBr that is oxidized and the uncertainties on spectroscopic measurements of volcanic gases.

The use of miniature UV spectrometers for SO₂ monitoring has proliferated over the past decade [Galle *et al.*, 2010]. SO₂ detection is relatively straightforward due to its high abundance in the plume. BrO and OCIO, however, are present in much lower quantities and the retrieval process can be technically challenging. This renders them unlikely candidates for operational monitoring at active volcanoes. In addition, Kern *et al.* [2009] confirmed that BrO is only formed during photolysis and is thus undetectable in measurable quantities at night. The formation of BrO from HBr, and indeed the exsolution processes involved in HBr emission are most likely complex and dependent on the behavior of the other volatile species in the melt as well as atmospheric factors. However, OP-FTIR measurements of HCl/SO₂ are practically challenging at SHV, particularly operationally, because the instrument is expensive to maintain and the measurements rely on solar occultation, which is labor-intensive. BrO abundance, like HCl, appears to be lower during eruptive pauses, and this suggests that BrO/SO₂ could provide important information about the presence of magma in the shallow system – and thus be of use for volcano monitoring. Sudden high BrO emissions may herald

a renewal of eruptive activity at Soufrière Hills Volcano. Nevertheless, at the present time these results are preliminary and further work is required to consolidate them.

OCIO has been detected in the plume at the SHV for the first time. It has only been detected in volcanic plumes previously at Mount Etna [Bobrowski *et al.*, 2007] and Puyehue Cordón Caulle [Theys *et al.*, 2014]. Its presence is a further indication of the high rate of HCl degassing, even during pauses, and of the reactive nature of halogen chemistry in volcanic plumes [Roberts *et al.*, 2009; Bobrowski *et al.*, 2007; von Glasow, 2010; von Glasow *et al.*, 2009].

Further studies involving the simultaneous measurement of dome/source temperature, aerosol content and, ideally, plume structure (e.g., using an SO₂ camera) would aid interpretation of halogen species in the plume. However, experimental studies are required to constrain the solubility of HBr in magmas and the usefulness of bromine species as monitoring aids. Given the findings of this study and those of earlier studies on bromine behavior [Alletti *et al.*, 2007; Bureau *et al.*, 2000; Villemant *et al.*, 2008], it is likely that bromine behaves significantly differently to chlorine in hydrous silicic melts. Experiments on natural samples of a range of compositions would aid interpretation of both models and field observations.

Additional studies to measure OCIO in plumes would also be beneficial, particularly where solar occultation provides the only practical means for measuring HCl in volcanic plumes by open-path Fourier transform infra-red spectroscopy. Finally, new modeling, particularly of the influence of aerosol and meteorological conditions on the retrievals and refinement of the DOAS method would be beneficial in reducing error on the measurements of trace gases.

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